The Olfactory Repellencies of Some Esters of Camphoric Acid to Culicine Mosquitoes : Insect Repellents and Attractants Part III

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な低級 alcohol ではないこと，又同時に第一菊酸は従来知られている pyrethrolone 及び cinerolone ester の外に低級 alcohol の ester としても存在する事がわかつた．

本研究を行うに当り御懇篤な御指導を賜つた京都大学化学研究所長武居教授，大野稔教授，井上雄三博士並びに西京大学野田万次郎教授に深甚の謝意を表す．又発表を許可された大日本除虫菊株式会社上山勘太郎社長に深謝する．

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Résumé

By means of paper chromatography tiglic acid was detected in dried pyrethrum flowers grown in Hokkaido district. This acid was shown to be characteristic for the Hokkaido-strain and to exist in the plant body as ester with higher alcohols. Actual separation of the acid from the flowers of Hokkaido-strain indicated the content of the free acid to be ca. 0.06% on dried flower.

Tiglic acid behaves substantially in the same manner as chrysanthemic acid and escapes the baryta-treatment in the course of pyrethrins-estimation, causing a serious error in pyrethrins-I content. Seil's and modified Seil's acidmetries as well as mercury reduction method, nowadays in current use, can not be relieved of this imperfection.

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12. 樟脳酸エステル類の家蚊に対する忌避効果について　忌避剤・誘引剤について　第3報.

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樟脳酸エステル類の防蚊効力について室内試験をおこない，皮膚塗付ならびに嗅覚試験の結果から，これらエステルの中でジメチルエステルがアカイエカ，コガタアカイエカの忌避剤としてもつとも有効であることを見出した．また，その効力持続時間は比較的短いが，樟脳白油もこれらの防蚊に役立つことを知つた．

In the previous report[3], Honda and Ikeda reported on the preparation and repelling properties of a number of derivatives of camphoric acid. The compounds have been tested for repellency by using only one species of mosquito, *Culex pipiens pallens* Coquillett as the test material. The compounds tested were camphor, camphor oil and six esters of camphoric acid.

In the tests, the authors recognized that dimethyl ester of camphoric acid and camphor oil were effective against *Culex pipiens pallens* in the olfactory tests.

This paper reports the further studies conducted thereafter with the same compounds in the skin applications and olfactory tests by using McIndoo's Y-tube against two species of *culicine* mosquitoes under the laboratory condition.

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Methods and Materials

The insects used were female adults of mosquitoes, *Culex tritaeniorhynchus* Giles and *Culex pipiens pallens* Coquillett.

Full grown larvae and pupae of these species were collected outdoors, and were reared up to adult in the laboratory. No foodstuff was given to adult for 1 day, then 20 females were used in each test.

The compounds adopted for test were camphor oil, and six esters of camphoric acid *viz.* di-*iso*-amyl ester (bp 205°—211°), dimethyl ester (bp 260°—265°), diethyl ester (bp 280°—282°), di-*n*-propyl ester (bp 300°—302°), di-*iso*-butyl ester (bp 315°—318°), di-*n*-butyl ester (bp 321°—324°). With relation to them the commonly known repellent, dimethyl phthalate (finished product for sale) was used. In order to avoid the effects of solvent etc., in all of the tests, compounds themselves were employed.

Olfactory test. The olfactometer used was the type according to McIndoo[1,4]. The Y-tube consisted of glass tubes 3 cm in diameter and 25 cm long in either side, and an insect entrance and air outlet were attached to the center of bifurcation. The set of bottles consisted of large one, 250 cc capacity, and a small, 50 cc capacity. The large bottle was used as the saturation chamber, while the small one was for regulating the speed of an air current. Each bottle was closed with a cork stopper, and these bottles were firmly connected by a short glass tube. The set was connected with the bore of the Y-tube in either side.

In the tests, the compounds were applied by 25 mg per filter paper of 9 cm^2. The impregnated paper was hung in the saturation bottle at once.

The criterion of repellency was based on the reaction of insects to odorous air diffusing through one arm from a saturation bottle containing test compound and odorless air through the other. Numbers of the mosquitoes reacted on odorous air were expressed by the percentage.

Skin Application. In the case of skin applications, 0.5cc of the compound was spread evenly over the forearm of the subject. The treated arm was exposed to caged mosquitoes for three minutes by every 30 minutes. Then, time of first confirmed bite was recorded. The criterion of repellency was based on the comparison of such protection time.

Results

The results of olfactory tests are given in Table 1. Dimethyl ester of camphoric acid was most effective in the tests. Among the esters of camphoric acid used, dimethyl form was most effective, and, diethyl was the next. But, comparing with that of dimethyl phthalate, other forms were far more effective. However, it must be considered that dimethyl phthalate used, in this test, was only a finished product for sale, so that the real value of this compound could not be estimated properly, and so the product, when used at a dose of 25 mg per test, had no responsive effect upon the mosquitoes.

Table 1. Comparative effectiveness of eight compounds against the female adults of *Culex tritaeniorhynchus* Giles in an olfactometer.

At 29°—30°, relative humidity 68—72%. Average of five tests.

Compound (Esters of camphoric acid)	Repellency Percent Time after application (hour)				
	½	1	2	3	5
di-*iso*-amyl ester	65	65	65	60	55
dimethyl ester	80	80	80	75	75
diethyl ester	70	70	70	70	65
di-*n*-propyl ester	60	65	60	60	55
di-*iso*-butyl ester	65	65	65	65	60
di-*n*-butyl ester	70	65	65	60	60
Dimethyl phthalate*	75	70	70	60	30
Camphor oil	100	90	70	45	10

* 250 mg was used per test, the dose corresponding to 10 times as much as that of the other compounds.

The results of skin applications with two candidates and dimethyl phthalate which have been picked up in the olfactory tests are given in Table 2. Dimethyl ester of camphoric acid was found to be superior or equal to dimethyl phthalate for skin application against two species of

Table 2. Comparative effectiveness of three compounds in skin applications against two species of mosquitoes. At 26°—30°. Average of five replications. P. E. s. : 0.6745σ.

Compound	Protection time in minute ± P. E. s.	
	Culex pipiens pallens (female)	*C. tritaeniorhynchus* (female)
Dimethyl ester of camphoric acid	132 ± 23	126 ± 17
Dimethyl phthalate	108 ± 11	114 ± 9
Camphor oil	72 ± 11	66 ± 17

mosquitoes.

Although camphor oil was outstanding in repelling mosquitoes in the early stage of application, its residual effect was of short duration.

Discussion

Among the compounds adopted, dimethyl ester of camphoric acid was most effective, and it was found to be superior to dimethyl phthalate against two species of *culicine* mosquitoes in both of the olfactory test and skin application.

Although camphor oil was inferior to the others in its residual effect, it was also effective for mosquito protection. The short duration of camphor oil may be due to the rapid evaporation and skin absorption.

It was interesting that the efficiency of dimethyl phthalate was more effective for mosquito protection in the case of skin application but was less in the olfactory test. However, this result should be confirmed for the pure compound, since the phthalate used was in commercial form. In the olfactory tests, dimethyl phthalate required about 10 times dosage to raise the repellency to equal the others, while in the skin applications there was little or no difference between series of camphoric acid esters in their effectiveness.

There is no doubt that it was connected with a matter of the reaction between skin and compounds, as has been suggested by Dethier[5].

Résumé

In the present paper, the author reported the further results with some esters of camphoric acid and camphor oil against two species of *culicine* mosquitoes in laboratory tests.

The repellent action of dimethyl ester of camphoric acid was most effective, even superior to dimethyl phthalate, against mosquitoes, *Culex pipiens pallens* and *C. tritaeniorhynchus*.

Camphor oil has outstanding effect in repelling mosquitoes. When applied to arm it retained 100% protection for more than one hour.

One interesting feature was about dimethyl phthalate, why its effectiveness in the skin application increased while does not in the olfactory test. The phenomenon might due to a matter, as was suggested by Dethier, of the reaction between skin and compounds.

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